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# The effect of nitrogen annealing on lithium ion intercalation in nickel-doped lithium trivanadate

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**Abstract** The communication reports an exploratory experimental study on the effects of nitrogen annealing on lithium ion intercalation in nickel-doped lithium trivanadate cathodic electrodes for lithium ion batteries. It shows good rate performance with discharge capacities of 348.6, 252.6, 191.9 and 96.7 mAh $g^{-1}$ at 0.2, 0.5, 1 and 5 C, respectively. Nitrogen annealing resulted in the formation of parasitic secondary-phase $LiV_2O_5$ and appreciably increased tetravalent vanadium ions compensated with oxygen vacancies, which would enhance the electronic conductivity and lithium ion diffusivity and promote the interface interaction and deintercalation process, and thus lead to the enhanced lithium ion intercalation properties. The possible impacts of the parasitic secondary-phase $LiV_2O_5$ on the lithium ion intercalation performance have also been discussed.

**Keywords** Nitrogen annealing · Nickel-doped lithium trivanadate · Oxygen vacancies · Parasitic secondary phase

## 1 Introduction

Although lithium ion batteries are one of the most successful energy storage technologies and have enjoyed widespread applications in the past 2.5 decades, search for better electrode materials for energy storage technologies with increased energy and power density with improved cyclic stability at a reduced cost and with earth abundant materials has only got increasingly intensified [1–3]. Lithium trivanadate ($LiV_3O_8$, denoted as LVO) has been studied in the past years since the first research of its lithium ion intercalation capability by Wadsley [4]. It is considered as a viable cathode for moderate-voltage lithium ion batteries due primarily to its relatively large reversible lithium ion insertion/extraction capacity [5, 6]. However, its low electronic conductivity ($\sim 10^{-6}$ S $cm^{-1}$) and lithium ion diffusion coefficient ($\sim 10^{-10}$ $cm^2$ $s^{-1}$) have hindered its practical applications [7–9]. Materials with appropriately designed and fabricated nanostructures with a large specific surface area have demonstrated to offer more active reaction sites for lithium ions and obviously possess shortened diffusion length in the insertion/extraction process and thus presented much improved cycling performance and rate capability [10]. Similar to other layer-structured cathode materials, the capacity fade of LVO is often attributed to structural changes, phase transition and surface changes [11]. Surface coating and passivation of nanostructured electrodes have demonstrated to be an effective approach for improving cyclic stability of LVO during the insertion/extraction of lithium ions [12–14]. Doping in cathode materials has also demonstrated to effectively improve electrochemical properties. For example, Mo-doped LVO cathode has better reversibility than pure LVO [15]. Similarly, Ni doping in LVO resulted in much improved lithium ion intercalation properties because low-valence-state Ni can introduce oxygen vacancies that provide the nucleating sites and ion diffusion path in the phase transition of electrode materials during the charge/discharge process [16].

SPECIAL TOPIC: Materials for Energy Conversion

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In addition to design and synthesis of nanostructures, carbon nanocoating and doping, the introduction of surface defects through controlled annealing in reducing gas is yet another approach to improve the lithium ion intercalation properties [17–20]. Liu et al. [19, 20] found that the presence of defects, such as $V^{4+}$, and associated oxygen vacancies could also improve the cycle life of LVO. The defects at the interface of LVO and electrolyte could possibly facilitate the phase transition during the insertion/extraction process due to modified surface thermodynamics [21, 22]. In addition, the presence of surface defects at LVO/electrolyte interface could preserve the integrity of cathode surface morphology, improving the cyclic stability of cathode materials [23]. Such surface defects in vanadium oxides can be readily introduced by annealing in an inert gas at elevated temperatures, such as in nitrogen gas at 300 °C [24, 25].

The present paper focuses on the effect of nitrogen annealing on the lithium ion intercalation properties of nickel-doped lithium trivanadate, a part of the efforts as to explore combined or even synergistic effects of doping and surface defects through annealing on the electrochemical properties, taking lithium trivanadate as a model system, as the impacts of nickel doping has been reported recently in a separate publication [16]. We first synthesized nickel-doped LVO (Ni-LVO) followed with annealing in air or nitrogen. The crystallinity, microstructures and lithium ion intercalation properties of the resulting Ni-LVO have been investigated, and the influence of the annealing atmosphere has been discussed. The experimental results revealed that Ni-LVO electrode annealed in nitrogen atmosphere exhibited improved electrochemical properties compared to that annealed in air, and the possible cause for such an improvement has been discussed.

## 2 Experimental

### 2.1 Material synthesis

All chemicals used in our work were analytical grade and were used without further purification. Previously reported procedure was modified to synthesize Ni-LVO [26]. $V_2O_5$, $CH_3COOLi·2H_2O$, $(CH_3COO)_2Ni·4H_2O$ and oxalic acid ($H_2C_2O_4·2H_2O$) were used as raw materials to prepare the precursor solution, oxalic acid acting as a both chelating and reducing agent. First, $V_2O_5$ and oxalic acid in a stoichiometric ratio of 1:3 were dissolved in deionized water under vigorous stirring at 400 r $min^{-1}$ at room temperature until the color of solution turned from yellow to blue, which indicates that the valance state of V transformed from +5 to +4 and that vandyl oxalate hydrate ($VOC_2O_4·nH_2O$) formed [27]. The reaction can be expressed as shown [28]:

$$V_2O_5 + 3H_2C_2O_4 \rightarrow 2VOC_2O_4 + 3H_2O + 2CO_2$$

Then, a certain amount of $(CH_3COO)_2Ni·4H_2O$ in which nickel accounts for 5 % of vanadium was added into the solution. The color of solution turned dark green. A stoichiometric amount of $CH_3COOLi·2H_2O$ was added, and then the mixture was vigorously stirred (600 r $min^{-1}$) for 1 h. Finally, the mixture was dried overnight in an oven at 80 °C to get the powder. The as-obtained powders were then annealed at 300 °C in nitrogen for 2 h at a temperature ramping rate of 2 °C $min^{-1}$ to get N-Ni-LVO. In contrast, we synthesized the powder and annealed at 300 °C in air in the same way to get A-Ni-LVO.

### 2.2 Material characterization

X-ray diffraction (XRD) analyses of the samples were conducted on a Marcogroup diffractometer (MXP21 VAHF) with a Cu-Kα radiation source ($\lambda = 1.54056$ Å). X-ray photoelectron spectroscopy (XPS) was performed on the Thermo Scientific ESCA Lab 250Xi using 200 W monochromated Al-Kα radiation. The 500-μm X-ray spot was used for XPS analysis. The base pressure in the analysis chamber was about $3 \times 10^{-10}$ mbar (1 mbar = 100 Pa). Typically the hydrocarbon C 1s line at 284.8 eV from adventitious carbon was used for energy referencing. The morphologies of samples were investigated by HITACHI SU8200 cold field emission scanning electron microscope (FESEM). The total surface area was determined using nitrogen sorption analyses via surface area and porosity analyzer (Micromeritics ASAP 2020 HD88, USA). For the mesopore surface area, pore volume and pore diameter, the Barrett–Joyner–Halenda (BJH) method was adopted, whereas the specific surface area and the pore volume of micropores were calculated using t-method.

### 2.3 Electrochemical characterization

Electrochemical tests were carried out using 2032 coin cells assembled in an argon-filled glove box in which both the content of oxygen and water were below 0.5 ppm (parts per million). To prepare working electrodes, a mixture of active material, carbon black and poly-(vinyl difluoride) (PVDF) at a weight ratio of 80:10:10 was pasted on an Al foil. The electrolyte was composed of 1 mol $L^{-1}$ $LiPF_6$ dissolved in a mixture of ethylene carbonate/dimethyl carbonate/diethyl carbonate (EC/DMC/DEC, 1:1:1 vol%, CAPCHEM). A Celgard polypropylene was used as the separator. To investigate the electrochemical properties of electrode materials, the half cells were adopted and lithium foil was used as the counter electrode.